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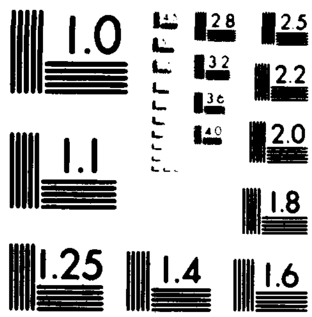

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Work dealt with photoelectron emission by liquids and solutions under irradiation in the ultraviolet and vacuum ultraviolet ranges. The two complementary aspects of this work were: (1) energy distribution curves of emitted photoelectrons, and (2) quantum yield of emission as a function of photon energies. A list of 19 Technical Reports and 14 publications is included.

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OFFICE OF NAVAL RESEARCH
Contract N00014-75-C-0397
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FINAL REPORT

ELECTRONIC PROCESSES IN POLAR LIQUIDS

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Department of Chemistry
New York, NY

May 10, 1982

This Final Report covers the work done with ONR support during the period January 1, 1975 to March 31, 1982 under contract N00014-75-C-0397.

I. SUMMARY OF WORK

Work dealt with photoelectron emission by liquids and solutions under irradiation in the ultraviolet and vacuum ultraviolet ranges. The two complementary aspects of this work are distinguished in the following discussion: (i) energy distribution curves of emitted photoelectrons, and (ii) quantum yield of emission as a function of photon energies.

A. Determination and Interpretation of Energy Distribution Curves of Photoelectrons

Instrumentation and methodology were developed for the determination of energy distribution curves with a rotating disk target at photon energies (vacuum ultraviolet monochromator) up to ca. 10.5 eV (report No. 2 listed in Sec. II) and with resonance lamps at fixed photon energies of 11.7 (ArI), 16.8 (NeI) and 21.2 (HeI) eV (report No. 4). Results and their interpretation are discussed in reports No. 1 to 6 and 8. Essential results include:

(i) The determination of the dependence of the cross section for photoelectron emission on photon energy (reports No. 1 and 2).

(ii) The observation and interpretation of emission of electrons which are unscattered in the liquid prior to emission into vacuum (report No. 5).

(iii) The determination of energies for photoelectron emission from second derivative curves (reports No. 3 and 8) and from energy distribution curves (reports No. 5 and 8).

(iv) Theoretical study of the transport of quasifree electrons in liquids in the diffusion limit (report No. 6).

B. Determination and Interpretation of Quantum Yield Spectra for Emission Spectra by Aqueous Solutions

Instrumentation and methodology were developed for the [illegible]nation of quantum yields for emission of photoelectrons by aqueous [illegible]ons as a function of photon energy up to ca. 11.5 eV (report No [illegible]7). [illegible]is development was essential to the subsequent, extensive experimental work and theoretical interpretation of results. Application to nonaqueous solutions of organic anion radicals was also investigated (report No. 10). A review of this work for the general reader was prepared (report No. 16). Essential results include:

(i) The experimental determination of threshold energies for photoelectron emission (report No. 11).

(ii) The basic relationship between the threshold energy and the free energies for emission and the subsequent reorganization process (reports No. 12 and 13).

(iii) Protonation energies of the radicals produced by photoionization of acids and their conjugate bases for water (report No. 15) and weak acids and bases and their ions (report No. 17).

(iv) Correlation of the kinetics of thermal electron transfer in solution or at electrodes with the energetics of photoelectron emission (report No. 18).

(v) The observation of unusual donor-acceptor electron transfer processes in the vacuum ultraviolet range and the development of a quantitative model based on a confined reaction volume (report No. 14).

(vi) The correlation between charge transfer spectra and the energetics of photoelectron emission (report No. 19).

II. TECHNICAL REPORTS

1. "Photoionization Spectra of Solutions as Obtained by Photoelectron Spectroscopy," L. Nemec, L. Chia and P. Delahay, June 1975.

2. "New Method for Photoelectron Spectroscopy of Solutions," H. Aulich, L. Nemec, L. Chia and P. Delahay, July 1975.

3. "Photoelectron Spectroscopy of Liquids: External Ionization Energies," L. Nemec, L. Chia and P. Delahay, January 1976.

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5. "Photoelectron Spectroscopy of Liquids up to 21.2 eV," L. Nemec, H. J. Gaehrs, L. Chia and P. Delahay, December 1976.

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7. "An Apparatus for the Measurement of Photoelectron Emission Current with On-line Computer Data Acquisition. Part I: Description of Cell and Operational Procedures," I. Watanabe, "Part II: Electronics, Computer Interfacing and Programming," J. B. Flanagan, March 1979.

8. "He(I) Photoelectron Spectroscopy of 1,2-Ethanediol: Comparison of Gas- and Liquid-Phase Spectra," L. Nemec, L. Chia, H. J. Gaehrs and P. Delahay, April 1979.

9. "Numerical Deconvolution of Photoelectron Spectra of Liquids," J. B. Flanagan, July 1979.

10. "Photoelectron Emission from Cyclooctatetraene Dianion Solution," I. Watanabe and J. Proscia, October 1979.

11. "Vacuum Ultraviolet Photoelectron Emission Spectroscopy of Water and Aqueous Solutions," I. Watanabe, J. B. Flanagan and P. Delahay, February 1980.

12. "Photoelectron Emission Spectroscopy of Inorganic Anions in Aqueous Solution," K. von Burg and P. Delahay, October 1980.

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14. "Non-adiabatic Capture of Mobile Electrons in Aqueous Solution," K. von Burg and P. Delahay, February 1981.

15. "Photoelectron Emission Spectroscopy of Liquid Water," P. Delahay and K. von Burg, April 1981.

16. "Photoelectron Emission Spectroscopy of Aqueous Solutions," P. Delahay, June 1981.

17. "Photoelectron Emission Spectroscopy of Weak Acids and Bases and Their Ions in Aqueous Solution," K. von Burg and P. Delahay, June 1981.

18. "Correlation Between Thermal Electron Transfer in Solution and Photoelectron Emission," P. Delahay, February 1982.

19. "Charge Transfer Spectra and Photoelectron Emission by Solutions," P. Delahay, April 1982.

III. PUBLICATIONS

1. L. Nemec, L. Chia and P. Delahay, J. Phys. Chem. 79, 1935 (1975) (report No. 1).

2. H. Aulich, L. Nemec, L. Chia and P. Delahay, J. Electron Spectrosc. 8, 271 (1976) (report No. 2).

3. L. Nemec, L. Chia and P. Delahay, J. Electron Spectrosc. 9, 241 (1976) (report No. 3).

4. L. Nemec, H. J. Gaehrs, L. Chia and P. Delahay, J. Chem. Phys. 66, 4450 (1977) (reports No. 4 and 5).

5. L. Nemec, L. Chia, H. J. Gaehrs and P. Delahay, J. Electron Spectrosc. 18, 169 (1980) (report No. 8).

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7. K. von Burg and P. Delahay, Chem. Phys. Lett. 78, 257 (1981) (report No. 12).

8. P. Delahay, K. von Burg and A. Dziedzic, Chem. Phys. Lett. 79, 157 (1981) (report No. 13).

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11. P. Delahay, Acc. Chem. Res. 15, 40 (1982) (report No. 16).

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13. P. Delahay, Chem. Phys. Lett., accepted (report No. 18).

14. P. Delahay, Chem. Phys. Lett., accepted (report No. 19).

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